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RAMAN, UV and IR Studies of the Nature of Phase Transitions in Polydialkylmetallanes, σ -Conjugated Organometallic Polymers of the type $[\text{RR}'\text{El}]_n$ (El=Si, Ge, Sn)

S.S. Bukalov and L.A. Leites

Scientific and Technical Center on Raman Spectroscopy RAS, A.N. Nesmeyanov Institute of Organoelement Compounds RAS, Vavilova str. 28, 119991 Moscow, Russia.

Polydialkylmetallanes are high-molecular-weight polymers with homoatomic main chain, consisting of either Si, or Ge, or Sn atoms. They are of interest not only from theoretical point of view because they behave as conjugated systems, exhibiting electron delocalization along the main chain formed by σ -bonds only, but also as perspective materials for modern microelectronics due to their unique electronic structure and industrially promising properties. Their potential industrial applications as photoresists, one-dimensional semiconductors, and materials for non-linear optics are mentioned in the literature. The most important feature of polydialkylmetallanes is that they undergo phase transitions (PT) of order-disorder type [1-3]. Three types of ordering can occur there by:

1. Intermolecular ordering, that is, a change in phase state. Polymetallanes can be amorphous, mesomorphic and crystalline.
2. Ordering of the main polymer chain; the latter can be either disordered statistically, or adopt various ordered conformations. A change in backbone conformation leads to an abrupt change in parameters of electronic absorption band (such a phase transition is called thermochromic) and in all important physical properties of the polymer.
3. Ordering of the side alkyl chains which can have various conformations due to hindered internal rotation about the C-C and C-El bonds.

It was of interest to elucidate the nature of PT of various polymetallanes as depending on the nature of R and El, using adequate and complementary methods of optical spectroscopy: UV and IR absorption spectra and pre-resonance Raman spectra, recruiting also DSC and WAXD techniques. As a result of studying numerous objects, it was found that *the three types of ordering are not necessarily interrelated*.

The most common are the so-called 'thermochromic phase transitions' (TPT), these are mostly transitions from crystalline phases, containing macromolecules with the most ordered (*all-A* or *all-T*) backbones and ordered alkyl tails, into mesomorphic state with partly disordered or helical backbones and disordered alkyl tails. These TPT involve all the three types of ordering

However, in some cases PT were observed that consist in expansion of the crystal unit only, without change in its symmetry. These transitions do not involve changes in the backbone conformation, whereas the extra volume of the unit cell allows "melting" of the side chains. For several polymetallanes, structural (not phase!) transitions were found which take place within mesomorphic or amorphous states and involve partial ordering of the main chain (thermochromism) without side chain ordering.

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